

Standard Operating Procedure for EPA's LBL Energy Dispersive X-Ray Fluorescence Spectrometry

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1.0 Introduction

1.1 Scope and Application

This SOP applies to XRF analysis of ambient aerosols sampled with fine particle ($<2.5 \mu$) samplers, dichotomous samplers, and the VAPS (versatile air pollution sampler). The data are intended for use in source apportionment research only.

1.2 Description of Spectrometer

The x-ray analyzer is an energy dispersive spectrometer custom made by Lawrence Berkeley Laboratory and possesses some features not found on commercially available machines. The tube is operated in a pulsed mode; it is actually turned off for $83 \mu\text{sec}$ after an x-ray is detected. This limits the maximum count rate to about 6.5 kHz - the optimum for the amplifier. This low count rate also reduces pulse pile-up, a phenomenon to be minimized which occurs in the detector at high count rates. The detector is a cryogenically cooled lithium-drifted silicon detector with an electronic guard ring for electronic collimation of x-rays. In addition to these unique features optimum excitation conditions are made possible by four fluorescers or secondary targets providing analysis capability for Al to Pb. The four fluorescers and the elements which they excite are: Ti, (Al to Ca); Co, (S to Mn); Mo, (Mn to Sr plus W, Au, Hg, and Pb), and Sm (Sr to La).

The machine is operated under control of an IBM PC/AT personal computer with a Nucleus Port PCA card which provides complete data acquisition and operation of the sample changer. All operational functions are controlled by computer menu (Appendix 9.4) allowing the operator control with only a few keystrokes.

1.3 Personnel Requirements

The minimum training required is a Master's degree in chemistry or physics with five years experience in energy dispersive x-ray fluorescence analysis of atmospheric aerosols and its associated data processing. Proficiency in using the DOS operating system, Fortran programming, and Lotus is required.

1.4 Precision and Accuracy

Precision varies with the element and concentration. At high concentrations (greater than $1 \mu\text{g}/\text{cm}^2$) a precision of 6% can be expected for elements analyzed by two fluorescers (S, Cl, K, Ca, Mn, and Sr). For all other elements at high concentrations a precision of 8.6% can be expected.

Based upon the analysis of NIST SRMS the accuracy is $\pm 10\%$. See Appendix 9.2 for the elements certified in these SRMs and Appendix 9.3 for typical analysis results of the SRMS.

1.5 Caveats

The spectrometer has an inherent contamination due to Sn (tin) which prevents quantitative analysis of this element at low ($<225 \text{ ng/cm}^2$) concentrations. This element may be reported as detected but if the concentration is less than the above stated amount the investigator should disregard it.

The type of samplers mentioned in Scope and Application must be operated in accordance with their instructions or severe errors in x-ray analysis may occur. For example, errors in flow rate will not just give erroneous volumes but will cause a more serious condition of altering the cut points upon which the coarse factor x-ray attenuations are based. If samples are intended for x-ray analysis then the sampling protocol must conform to the constraints inherent within the method.

2.0 Sample Preparation, Storage, and Tracking

2.1 Sample Log-in Procedures

When samples are received for analysis they are assigned an XRFID which is logged in the form entitled ASSIGNMENT OF XRF IDs. (See Appendix 9.8 for an example of this form) . The IDs are structured so that the first three digits represent the study name and the fourth digit represents a sub-study. A sub-study can accommodate a maximum of 72 samples and there are 10 possible sub-studies in each study. Each study name is assigned an archive ID which refers to a physical Bernoulli disk on which the data are archived.

2.2 Sample Preparation

Filter samples are received in individual plastic containers packaged for delivery in the postal delivery system. After receipt the filters are unpacked and arranged on the sample preparation table so as to match the physical samples with the accompanying field data sheets. This will ascertain that a complete data set has been received and will check for missing samples. The individual samples are then unpacked and checked for any invalidating conditions such as holes, tears, or a non-uniform deposit, any of which would prevent quantitative analysis. If such a condition is found the sample is invalidated and noted on the appropriate xrf data entry form corresponding to the type of sample. See Reference 2 in Section 8 for an explanation of the types of data entry forms used.

All filter samples received for analysis are removed with tweezers from their container and placed in a two-part sample frame (see drawing in Appendix 9.11) with the deposit side facing away from the retaining ring. The spacer ring shown in the drawing is needed to provide the correct spacing. When mounting filters such as Teflo which are already bonded to a supporting ring the spacer ring is not needed. The retaining ring is snapped into place to firmly hold the filter. Note that in the above described geometry the sample deposit is facing IM during analysis. The sample ID is written on a pressure sensitive label and fixed to the recessed portion of the retaining ring and the assembly is placed in the slot of an Argus slide tray corresponding to an entry line on the field data entry form (see Section 4.1 on Field Data Entry). A pair of slide trays is then placed in the spectrometer sample changer for analysis.

2.3 Sample Status and Tracking

After the sample IDs have been placed on the frame and the trays loaded the samples are ready for analysis. A scheme has been devised whereby the run progress can be tracked through the process and afterwards its storage location identified. Since several runs of samples may simultaneously be in different stages of the analysis process an XRF RUN STATUS LOG form is used. This form consists of a check list in which the completion dates are entered for the various steps in the process (See Appendix 9.8 for an example of this form). Briefly, the check list is: XRFID (the four-digit number identifying the run of samples); STUDY NAM (a descriptive name assigned by the operator); XRF DATE (the date the XRF measurement was started); CARD DATE (the date the field data entry was completed and verified); LSO DATE (the date the least squares analysis was performed on the spectral data); QC CHECKS (the later of the dates of checking the run-time QC data and the analytical results on the SRMS); IPAB XFER (date of uploading results to the SARB data base); HARD COPY LIB (the type/format of data on file in the data library, either ng/m³ or ng/cm² format); HARD COPY FIL (type of data format on file in run-time I/O file cabinet); ARCHIVE DATE (date data were archived).

After completion of analysis the trays of samples and a copy of the field data are placed in plastic bags and stored by XRFID for an indefinite period of time in the wall cabinets located in S242J. If samples are to be removed for scanning electron microscopy or returned to investigators there is a log form entitled SAMPLE CHECK OUT LOG in which the IDs of the samples removed are recorded along with date and signature. (See Appendix 9.8 for this form).

3.0 Spectrometer Operation

3.1 Preparation for Operation and Shutdown

All spectrometer operations are performed by an IBM PC/AT computer controlled interface. When the computer is first turned on each day, two procedures must be performed in order to initialize the spectrometer. These are: (1) position the first fluorecser in proper alignment with the sample and detector and (2) position the sample rotor in the load position to accept the first sample from the sample changer. To execute these procedures do the following:

To locate fluorecser:

1. Select 2 from menu (see Appendix 9.4).
2. Press ENTER three times on keyboard and wait until resulting process is complete
3. Press ESC twice on keyboard.
4. Enter Y at prompt. Menu reappears
(Fluorecser is now located)

To find load position:

1. Select 1 from menu
2. Wait for FPLOT screen and enter 8
(Load position is now located)

The settings for the helium flow, the front panel controls, and the shutdown sequence are explained

in Appendix A of Reference 1 (see Section 8).

3.2 Gain and Baseline Adjustment

Before the run of unknowns the gain and baseline must be checked. This will assure that the x-ray energies are assigned the correct channel numbers. Refer to Appendix A of Reference 1 for this procedure.

3.3 Run Options

Procedure 5 from the menu (see Appendix 9.4) is used to run samples. There are four run options depending upon what kind of samples are being run. These options are:

1. Unknowns and QC standards
2. Unknowns only
3. Blanks and QC standards
4. Shapes and QC standards

Option 1 is generally used to measure all unknowns. The least squares spectral processing program requires that QC standards and unknowns be processed in the same run so this option is essential if subsequent spectral analysis is desired. Option 2 is used in special cases in which it is necessary to add sample spectra to an existing run. Option 3 measures blanks for background spectra. Option 4 measures shape standards for calibration purposes (See Section 5.4). The keyboard input response required for each of these options is addressed in Appendix E of Reference 1 and will not be elaborated upon in this document.

After the completion of Options 1, 3, or 4 the run-time QC files shall be updated (See Section 6.2 for a description of run-time QC). To update the files containing the data from run-time QC follow the instruction below.

1. Make sure the run-time quality control criteria are met. (See section 6.4)
2. Select Procedure 21 from the menu (Appendix 9.4)

This will put the run-time QC data from the run into cumulative files named C:\XRF\XRFRUN\XQC\ARCHxx.NEW where xx is the element name. See Section 6.6 on Control Charts for the use of these files. The hard copy of the run-time printout and a copy of the field data (see Section 4.1) are filed by XRFID in the run-time I/O file cabinet.

4.0 Data Analysis and Reporting

4.1 Field Data Entry

Data entry is accomplished by using one of four Lotus spreadsheets depending upon which kind of sampler was used to collect the sample. Use of these spreadsheets is explained in Reference 2 (see Section 8.0). Great emphasis shall be put on careful field data entry because it is the most error prone step in the analysis process. After data entry is completed and verified (see Section 6.5) two hard copies are made of the card file. One copy is filed in the run-time I/O file cabinet, one copy is

put in the plastic bag with the trays of samples, and the original is filed in the XRFID Assignment notebook.

4.2 Least Squares Analysis

The pulse height spectrum for each sample is deconvoluted into its constituent elemental spectra by a linear least squares algorithm. In this process standard elemental shape spectra determined during calibration (see Section 5.4) are fitted to the unknown spectra. A set of coefficients determined by minimizing chi-square are proportional to the concentration of a given element. Thus, through the calibration sensitivity the concentrations are determined. It is not within the scope of this SOP to describe this process in any detail. Readers wishing a more detailed account should refer to Reference 3 in Section 8.

All of the processing options for least squares analysis such as selection of the shapes, background, attenuation factors, sensitivities, and field data are contained in the card files. To perform least squares analysis on a run of unknowns follow the three instructions below:

1. Select Procedure 6 from menu (see Appendix 9.4).
2. Enter four digit xrfid as called for. (Processing of spectra will take up to 20 minutes for a full 72 sample run).
3. Select Procedure 22 from menu to check SRM data results.

The three output files LSONnnn.NG3, LSQnnnn.CM2, and IPABnnnn.DAT are created in the same directory as the unknowns. (Refer to Reference 2 for more details on naming conventions and file structure). Since SRM spectral data is processed with the unknowns the operator should at this time add the current run's SRM data to the SRM data archive (in Step 4 below) if the SRM data passed the acceptance criteria.

4. Select Procedure 10 from menu to archive SRM data.

This will update the SRM data in a cumulative file called
D:\XDATA\ARCHIVE\SRM.DAT for charting purposes described in Section 6.6.

4.3 Detection Limits

The detection limits are determined by propagation of errors. The sources of random error which are considered are: (1) calibration uncertainty ($\pm 5\%$); (2) long-term system stability ($\pm 7\%$); (3) peak and background counting statistics; (4) uncertainty in attenuation corrections; (5) uncertainty in overlap corrections; (6) uncertainty in flow rate; and (7) uncertainty in coarse fraction due to flow fraction correction (dichotomous samples only). For typical 1 σ (68% confidence level) detection limits on a Teflo blank for fine particles and a Nuclepore blank for coarse (2.5 μ - 10 μ) particles see Appendix 9.6. These detection limits are defined in terms of the uncertainty in the blank. This ignores the effect of other elements which generally is small except for the light elements (potassium and lower) where overlapping spectral lines will increase the detection limit. Note: The difference in the detection limits between the two filters is due more to the difference in sensitivity to fine and coarse particles and less to the difference in filter material. Higher confidence levels may be chosen for the detection limits by multiplying the 1 σ limits by 2

for a 2 σ (or 95% level) or by 3 for 3 σ (or 99.7% level).

4.4 Data Reporting

There are five output files created for data reporting depending upon the reported concentration units and format. Three are created by the least squares analysis program (see Section 4.2) and two are created upon request. The files are named so as to reveal their contents. They are: (1) the LSQnnnn.NG3 file containing data as ng/m³, (2) the LSQnnnn.CM2 file containing data as ng/cm², (3) the IPABnnnn.DAT file which is a special format for uploading data to the branch data base, (4) the LSQnnnn.SEM file which is a companion file to scanning electron microscopy in which the elemental concentration in ng/cm² has been converted to that of the most likely chemical species, and (5) a Lotus spreadsheet created by the end user from the LSQnnnn.NG3 file. Reference 2, Section 8.0 gives the procedures for creating hard copies of the first two files and the uploading procedure for the third file. The fourth file is created from the LSQnnnn.CM2 file for fine/coarse paired filters and so is available only in concentration units of ng/cm². To create this file follow the instructions below.

1. Run program SEMOUT. (This will execute from any directory).
2. Enter four-digit XRFID
3. Output file is in directory D:\XDATA\Xnnnn, with name LSQnnnn.SEM.

The fifth type of output file is intended for creation by the end user because there are some customized choices which one must make and it is assumed that the end user is the appropriate person to make these choices. See Appendix 9.12 for instructions for creating the Lotus spreadsheet version of the LSQnnnn.NG3 file.

Hard copies of LSQnnnn.NG3 and LSQnnnn.CM2 are filed in the data library located in room S242J for use by branch personnel. (See Appendix 9.5 for selected examples of reports).

The uncertainty reported with each concentration is a 1 σ (68% confidence level) uncertainty and is determined by error propagation described in Section 4.3. Elements with concentrations below three times the uncertainty are flagged with an asterisk (*) on the printed record. If the true elemental concentration is zero then the fitting procedure implies that negative and positive results are equally probable. Therefore negative numbers may be reported.

4.5 Data Archiving

A directory is created for each XRFID at run-time. In these directories are located all the raw spectra files, field data or card files, and final data processed into report format. For a run consisting of a full 72 samples the directory size is considerably larger than typical diskette size of 1.2 megabytes. To store all the contents of the directory and remove it from the hard disk, an archiving procedure is used which compresses the data on Bernoulli cartridges and backs up the same on diskettes. Refer to Reference 2, Section 8.0 for the archiving and de-archiving procedures.

5.0 Calibration

Calibration is by far the most complex task in the operation of the XRF facility. There are many steps in the process which are best left to personnel with sufficient experience in energy dispersive x-ray fluorescence analysis to understand the process. Heavy use is made of References 1 and 5 in Section 8.0; it is the intent of this section to present the steps in a sequential organized manner and refer the operator to the references for details.

There are several steps in the process which require manual entry of data (see Sections 5.7 and 5.8). These are error prone procedures which require careful attention. Gross entry errors may eventually become obvious but small ones may go undetected so it is essential that the entered data be carefully checked against the original records.

Calibration is performed only when a change in fluorescours is made or a serious malfunction occurs requiring significant repairs. The spectrometer has gone as long as two years between calibrations without persistent failures in the parameters monitored by the quality control procedures. It takes approximately two weeks to complete a calibration.

5.1 Source and Description of Calibration Standards

There are three types of calibration standards. One type consists of thin films deposited on Nuclepore film substrates (Micromatter Co., Eastsound, WA). These standards are available for almost all the elements analyzed ranging in atomic number from 13 (Al) to 82 (Pb) with deposit masses gravizatrically determined to $\pm 5\%$. Another type consists of polymer films that contain known amounts of two elements in the form of organo-metallic compounds dissolved in the polymer (Reference 4, Section 8.0). These standards are available for elements with atomic numbers above 21 (titanium and heavier). The third type are sulfur thin film Standard Reference Materials available from NIST and certified for sulfur only. They are used only for calibration and not for quality control. Some standards have high inherent volatility and do not serve well as calibration standards. These are Se, Br, Hg, and elemental As. See Section 5.7 for the calibration approach to determining the sensitivity for these elements. All standards are mounted in frames in the same manner as unknowns, stored in Argus slide trays, and sealed in plastic bags until needed for calibration.

The same set of standards is used every time the spectrometer is calibrated. The standards are sufficiently durable to last many years, however occasionally one must be replaced due to accidents in handling. To check standards against degradation we periodically participate in audits. (See Appendix 9.14 for an audit report). A listing of the set used in the last calibration (October 1991) is given in Appendix 9.9.

5.2 Gain and Baseline Adjustments

To begin the calibration the gain and baseline are adjusted just as is done before any measurements (See Section 3.2). *However, this adjustment of the gain and baseline must not be changed until all measurements of background and shapes standards are completed!* This may take five days, so it is wise for the operator to ascertain that the gain and baseline are stable prior to beginning calibration by making several short runs of samples (Procedure 5 in menu, Appendix 9.4) over a 24 hour period. If the run-time quality control results are stable, calibration can begin.

During the period that the background and shapes are being measured (see Sections 5.3 and 5.4) the run-time quality control results are generated in hard copy form. The operator should have about seven to 10 runs of the run-time QC results accumulated over the period of background and shapes measurement *during which no adjustments were made to the gain and baseline*. The results for all parameters measured are entered into the spreadsheet C:\LOTUS\QCTGT91.WK1 where the averages are computed. These averages form the new basis for run-time quality control target limits for future measurements. To instate the new limits the operator runs the program C:\XRF\XRFRUN\CALIB.EXE and follows the instructions to enter the data. (See Reference 5 pages 47, 59, and 73 found in Section 8.0). The data are then entered manually into file C:\XRF\XRFRUN\QCTOLOOI.DAT.

5.3 Background Measurement

Thirty-six clean Teflo blanks are kept sealed in a plastic bag and are used exclusively for background measurement. Blanks are analyzed using Procedure 5 from the menu (Appendix 9.4) with run Option 3. (see Section 3.3). This will put the spectra in the directory D:\XDATA\BLANK\ with names Blnnnpp.XRO. Procedure 11 from the menu is used to sum blanks on a channel by channel basis. This procedure is self explanatory but for more information refer to Section 4.0 of Reference 1 found in Section 8.0 of this SOP for instructions. Note: the operator may find that it is best to preview the spectra for each fluorescer before selecting the spectra to be included in the sum in order to know which filters are contaminated. This can be done with Procedure 11 - just execute the procedure twice, once for a preview and again for final selection. If contaminated filters are found they are excluded from the sum. When the procedure is complete there are four background spectra files called 'SUMBLANK' files - one for each fluorescer and with names SBnnnn.BFj where "j" is the fluorescer number. These files reside in the D:\XDATA\BLANK\ sub-directory.

5.4 Shape Standards

The shapes standards are thin film standards consisting of ultra pure elemental materials for the purpose of determining the physical shape of the pulse height spectrum. For this purpose it is not necessary for the concentration of the standard to be known - only that it be pure. A slight contaminant in the region of interest in a shape standard can have serious effect on the ability of the least squares fitting algorithm to fit the shapes to the unknown. For this reason the Se, Br, Hg, and elemental As standards, whose compounds are volatile, are kept in separate plastic bags to prevent contamination of other standards. For most of the shape standards calibration standards are used because the calibration standards are quite pure. However, a few of the calibration standards have impurities which render them ineffective as shapes standards even though they are adequate for calibration. In these cases aerosol standards have been prepared for exclusive use as shape standards. The shape standards are kept in trays and sealed in plastic bags until needed.

The shape standards are analyzed using Selection 5 from the computer menu (see Appendix 9.4) with Option 4. This will store the raw spectra in the sub-directory D:\XDATA\SHAPE\ with the file names STnnnnpp.XRO. After shapes measurement the shape spectra must have the background subtracted from them using Selection 12 from the computer menu. This is an interactive procedure and is described in Section 4.0 of Reference 1. found in Section 8.0 of this SOP. Guidelines for subtraction of the SUMBLANK files from the shape spectra are also given in Reference 5, page 20. The background subtracted spectra are given file names Bknnnn.SDj,

where "j" refers to the fluorestor number.

The channel limits which define the location of the elemental peaks in the spectrum are selected next. This is done by viewing the spectra BKnnnn.SDJ with Selection 13 from the computer menu. Guidelines for choosing the channel limits are given in Reference 5, page 20. Upon selection of the limits they are put into the file C:\XRF\CALIB\SHCARD.CD manually via an editor. Refer to Reference 5, page 23 for the structure of this file.

The shapes files C:\XRF\CALIB\SHAPES.SHn are created next by running the program C:\XRF\CALIB\SHAPES.FOR using file SHCARD.CD as the input file. In addition to shapes data the shapes files contain the elemental sensitivities which at this point in the calibration process are all set equal to 1000. They will be changed to correct values once the calibration standards are measured. These shapes files must be copied to the D:\XDATA\SHAPE sub-directory.

5.5 Determine Fraction of Measured K Lines to Total K Lines

In the calculation of the sensitivity, a physical model is used in which it is assumed that all of the K α , K β and escape peak x-rays are measured. This is not always the case as sometimes the K β and escape peaks are excluded as is typical at fluorestor boundaries. In such cases as these, the ratio of measured lines to total lines must be determined for each element. This is done by measuring each applicable element using FLOT from the computer menu (Appendix 9.4) and is described in Appendix A of Reference 1 found in Section 8.0 of this SOP. Reference 5, pages 52 to 57 gives a detailed account of which elements require this measurement and the results from the last calibration.

5.6 Measure Calibration Standards

The calibration standards are measured as described in Section 3.3 using run Option 1. At this point in the calibration the new quality control tolerance limits have been determined and instated in the proper file and the background and shapes standards have been measured, so the gain and baseline can now be adjusted if necessary to meet the new criteria.

5.7 Calculate Sensitivities

The sensitivities are calculated using a model based on the fundamentals of the x-ray physics process as well as measurements on the calibration standards. This approach allows the calculation of sensitivities for elements for which there are poor or no standards such as volatile ones like Se, Br, Hg, and elemental As as well as improving on elements with good standards. See Section 4.0 of Reference 1 found in Section 8.0 of this SOP for more details on the model and approach.

The spectra from the calibration standards are analyzed as described in Section 4.2 using the newly determined shapes files D:\XDATA\SHAPE\SHAPES.SHn. With the sensitivities set equal to 1000 in these files the results of analysis will be in terms of intensity rather than concentration in the output file LSQnnnn.CM2 under the columns entitled "RAW DATA". A hard copy of this file must be printed because the intensity data must be entered by hand into file C:\XRF\CALIB\FACTOR\XXXXXX.YYY where XXXXXX.YYY is an operator-defined file

name. (Refer to file CAL91C.DAT in the same directory-for an example of the format of the data). The operator then runs program C:\XRF\CALIB\FACTOR\XRFCAL.EXE and specifies XXXXXX.YYY as the input file to calculate the sensitivities and write them to file XRFCAL.OUT. Refer to Reference 6, Section 8.0 for the contents of XRFCAL.OUT from the latest calibration period. This file shows the deviation of each standard from the fitted curve and a value of chi-square for each fluorescer. If the deviations and chi-squares differ significantly from previous values then the operator must determine which standards are causing the effect and assign a higher uncertainty (or weighting) to them, or replace or remove them if necessary. The fitted sensitivities must then be entered by hand to the shapes files D:\XDATA\SHAPE\SHAPES.SHj to create the final version of the shapes files for subsequent runs. Refer to Reference 5, page 29 for an example of a shapes file.

5.8 Overlap Coefficients

The final step in calibration is assembling the necessary data to compute the overlap coefficients. To obtain this data the operator reprocesses the calibration spectra with the newly fitted sensitivities in the shapes files. The elements which are affected by overlapping elements are contained in spreadsheet file C:\LOTUS\CAL91\OLAP91.WK1 along with all the necessary data on each standard. Refer to Reference 6, Section 8.0 for the contents of the spreadsheet from the latest calibration data. The data from the least squares analysis of the calibration standards which is to be entered manually into this spreadsheet is contained under the column "RAW DATA" in the LSQnnnn.CM2 file. The calculated overlap coefficients and their uncertainties are then manually entered into the file D:\XDATA\ATTEN\OLAP91.LBL and D:\XDATA\ATTEN\UOLAP91.LBL.

6.0 Quality Control

6.1 Description of QC Standards

Along with the two trays of samples analyzed in each run there are two sets of six quality control standards that are permanently mounted in the sample changer. One set, called the bottom standards is analyzed at the beginning of each run and the other set, called the top standards is analyzed at the end of each run. One standard in each set, is an NIST SRM on which a quantitative analysis is reported and all the others are used as a run-time evaluation of the operating condition of the spectrometer. A description of these standards follows:

Bottom standards	
ID	Description
Al 58	MicroMatter Al film on Nuclepore filter
S NTHP20	Sulfate aerosol on Teflo filter
VK AER01	Vanadium & potassium aerosol on Teflo filter
FePb 39b	Polymer film containing Fe & Pb
ZrCd 38y	Polymer film containing Zr & Cd
SRX 1833	NIST SRH certified for Si, K, Ti, Fe, Zn, Pb

Top standards	
ID	Description
Al 50	MicroMatter Al film on Nuclepore filter
S NTHP19	Sulfate aerosol on Toflo filter
VK AER02	Vanadium & potassium aerosol on Teflo filter
FePb 31a	Polymer film containing Fe & Pb
ZrCd 40a	Polymer film containing Zr & Cd
SRM 1832	NIST SRM certified for Al, Si, Ca, V, Mn, Co, Cu

6.2 Run-time Quality Control

During a run of samples one gets a hard copy printout of the results of the measurements on the top and bottom QC standards (see Appendix 9.7 for a typical run-time printout). The parameters which are checked and their significance are: peak areas (monitors change in sensitivity), background areas (monitors contamination or background changes), CHAN, or centroid (monitors gain and baseline adjustment to insure that spectra are assigned the correct channel), and FWHM, (monitors degradation of the detector resolution). These four parameters are measured for elements ranging from aluminum to lead and include atmospheric argon. The acceptable ranges for these parameters are based on averages and allowable uncertainties determined during calibration. The allowable uncertainties for elements other than argon are:

Peak area:	± 7%
Background area:	± 30%
Centroid:	± 3% of FWHM
FWKM:	± 6%

Any deviation from these established limits is automatically flagged at run-time for rapid and easy recognition. This process results in 48 measurements made both before and after unknowns are analyzed for a total of 96 measurements to assure proper operating condition of the XRF spectrometer.

6.3 Quality Control with Standard Reference Materials

In addition to the run-time quality control procedure above the analysis results of the SRMs are included in all data reports. The value reported is to be compared to the NIST effective value. (see Appendix 9.2 for explanation of effective value and 9.3 for results of SRM analysis). This provides an overall check of the spectral processing program for the elements which are certified in the standards. The sole purpose of the SRMs is to provide a quality control measure; the standards are not used for calibration.

6.4 Acceptance Criteria and Procedures for Corrective Action

An entire XRF run is invalidated if more than two of the measurements on the 12 QC standards exceed the allowable uncertainties as described under the Run-time Quality Control section or any one measurement lies more than 20% outside of the limits. There is a special case in which three failures are allowed and that is if one of the failures is due to arithmetic rounding off. The acceptance criteria of results 4, for the elements certified in the SRMs is that the uncertainty intervals for the analytical results and the certified values should overlap each other.

If a run is invalidated due to centroid failure it can be corrected by adjusting the gain or baseline. Correction for this is described under Gain and Baseline Adjustment in Spectrometer Operation (Section 3.2). Failure due to a decrease in peak areas is usually due to dust on the detector window which is remedied by gently blowing the area clean. Persistent high or low peak areas not responding to the above measures indicate need for recalibration. Failure due to a high Ar peak indicates that the helium flushing system is low on helium and atmospheric Ar has entered the measurement cavity. Replacing the empty helium bottle will remedy this. After the necessary adjustments are made the run is repeated.

6.5 Field Data Entry Checking

Field data consists of sample IDs, flow rates, sampling times, sites IDs, and other vital information. These data are essential for proper data processing to produce the necessary information for the investigators. To this end it is essential that a method be in place to insure that field data is accurately entered into the data processing program.

There are four LOTUS spreadsheets which are used for data entry depending on which type of sampler was used. These spreadsheets and their use are explained in Reference 2 (see Section 8.0). Data are entered into these spreadsheets from the corresponding field data sheet either by manual or electronic transfer. After manual entry the spreadsheet data are compared with the data on the entry form. If the data agree with that on the data form, a printed copy of the spreadsheet is signed to indicate its validity and is filed in the XRF ID assignment notebook.

Electronic field data entry is used when field data is submitted on diskettes. For sufficiently large field data sets it is usually advantageous to write a computer program to extract the data and render it in a format suitable to the corresponding LOTUS spreadsheet. There is no protocol for such data transfer because the field data may come in a different format for each study which means that a different program must be written for each case. Nonetheless such electronic transfer is still less error prone than direct manual entry. For electronic field data entry the data for the first and last samples in the spreadsheet and randomly selected data from the middle of the spreadsheet are compared to the samples in the corresponding submitted data. If the data agree then a printed copy of the spreadsheet is filed in the XRF ID assignment notebook.

6.6 Control Charts

Control charts are maintained on both Standard Reference Materials and the top QC standards. The top QC standards are chosen for plotting because they are measured at the end of the run. Use of the bottom standards may bias the results because they are analyzed at the beginning of the run immediately after the gain and baseline adjustment (see Section 3.2) and therefore may have a greater probability of being in control.

Two sets of control charts are maintained, one set is based on the run-time QC data and consists of plots of peak area, background area, centroid, and FWHM for the following elements: Al, Si, S, K, Ca, V, Fe, Zr, Cd, and Pb. Each parameter is divided by its mean which was determined during calibration and this normalized value is plotted against a chronological run number to produce an historical record of performance. The control chart upper and lower limits are based on experience and are: peak ($\pm 7\%$); background ($\pm 30\%$); FWHM ($\pm 6\%$); centroid ($\pm 3\%$ of FWHM). The second set of control charts is based on actual least squares analysis of SRM Spectra for the elements certified in both SRKs (Al, Si, K, Ca, Ti, V, Mn, Fe, Co, Cu, Zn, and Pb). Here the

measured concentration is divided by the effective value and this ratio is plotted as a function of time. The control limits are not set at a fixed level but are based on overlapping uncertainties and are computed in the following manner: Assume an element in the standard is certified at a concentration of 1000 ± 120 ng/cm² and upon analysis the concentration was determined to be 850 ± 100 . The upper and lower control limits are $(1000+120+100)/1000$ or 1.22 and $(1000-120-100)/1000$ or .78, respectively. The control limits vary slightly because the uncertainty of the analytical results vary too. The plots for both sets of control charts will be in effect until recalibration. Ratios rather than absolute magnitudes are plotted to allow a more rapid assessment of relative change.

The collection of the run-time QC data is explained in Section 3.3 (Run Options) and the saving of SRM analysis results is explained in Section 4.2 (Least Squares Analysis). The instructions for creating the control charts for these data sets for subsequent viewing and retrieval are given below.

1. Copy files C:\XRF\XRFRUN\XQC\ARCHxx.NEW to C:\QCXRF directory
2. Copy file D:\XDATA\ARCHIVE\SRM.DAT to C:\QCXRF directory
3. Run LOTUS 123
4. Retrieve C:\QCXRF\START.WK1

This automatically creates all graphs as .PIC files for viewing or printing with LOTUS PRINTGRAPH. See Appendix 9.10 for selected examples of control charts and Section 6.2 for the significance of the parameters plotted.

6.7 Self Consistency Checks

There are certain properties that ambient aerosols possess which can be checked to ascertain the validity of the analysis. One of these properties is that coarse fraction calcium is expected to be greater than fine fraction calcium. If analysis results do not confirm this then it is indicative of a sampler malfunction and such is automatically noted on the data report.

A second self-consistency check involves mass balance between the xrf-determined concentration and the gravimetric measurements. The elemental concentrations are converted to chemical compound concentrations based on a species most likely to be present. The mass determined by XRF plus the light element mass such as carbon and nitrogen determined by companion methods should closely match the gravimetric mass. This information is useful to the investigators but is not routinely included in the data report.

6.8 Goodness-of-Fit Measurements

The fitted spectrum and the measured spectrum are compared and a value for chi-square is calculated and reported with the data. Chi-square values that are much larger than 1.0 indicate a problem in the fitting procedure. Changes in detector resolution or gain in the amplifier produce large values for chi-square; however such changes would be detected by their run-time quality control procedure (see Section 6.2). Also, large chi-square values can accompany results for heavily loaded filters even though the relative errors are typical. In addition, elements analyzed by the titanium fluorescer may experience large chi-square values due to interferences from

overlapping elements. Chi-square is a more useful measure of goodness-of-fit for the other fluorescers for this reason.

To acquire more information about fitting problems the fitted spectra can be viewed on the screen or a hard copy printed. Such plots can be compared to the unknown spectra, background spectra, or to the library shape standards to help elucidate the suspected problem. Various statistics such as the correlation coefficient can be calculated on the fitted and measured spectra as a additional measure of the goodness-of-fit. See Appendix 9.13 for an example of the fitted spectrum superposed on its measured spectrum along with the associated statistics. The fitted spectra are stored in the directory D:\XDATA\LSQFIT. Refer to Section 3.0 of Reference 1 found in Section 8.0 of this SOP for instructions for plotting spectra.

6.9 Audit Reports

From time to time the x-ray facility is audited by in-house Quality Assurance personnel. Refer to Appendix 9.14 for the latest report.

7.0 Preventive Maintenance

7.1 Liquid Nitrogen Filling Procedure

The liquid nitrogen dewar shall be filled weekly. A check of the liquid nitrogen log will show the last time it was filled as well as the purchase order number and vendor from whom to order a replacement tank. A filled dewar will last approximately eight to nine days but safe practice calls for weekly filling.

1. Make sure x-rays are off (refer to shutdown procedure in Appendix A, Reference 1 found in Section 8.0 of this SOP) and open rear cabinet behind the sample changer.
2. Remove argon bag and place temporarily in safe place where it will not attract dust.
3. Open black-handled valve.
4. Enter time of day in log book under "BLOW" and quickly proceed to liquid nitrogen tank outside lab and open the valve marked "LIQUID".
5. Go behind spectrometer and wait three to four minutes and open blue-handled brass valve to allow liquid nitrogen to flow into the dewar. Then close the black-handled valve. Enter the time at which the blue-handled valve was opened under "FILL".
6. The filling will take approximately six to nine minutes. During this time locate the protective glove near the log book and wait until overflow occurs from the neck of the dewar. When overflow occurs turn off the blue-handled valve and quickly go (with glove) to the liquid nitrogen tank and turn off the valve marked "LIQUID". Enter time at which blue-handled valve was turned off in log book under "STOP" and the total filling time under "t" (Should filling take longer than 10 minutes turn off the blue-handled valve and proceed as if overflow has occurred.)

7. Wait approximately two hours for the frozen condensation on the lines to evaporate and reinsert argon bag and close and lock rear cabinet.

7.2 Argon Bag Filling Procedure

The argon bag on top of the conical x-ray shield shall be filled as needed - usually once or twice a week.

1. Make sure x-rays are off (refer to shutdown procedure in Appendix A, Reference 1 found in Section 8.0 of this SOP) and take argon bag to argon tank.
2. Attach hose and fill. Rate of filling and amount of fill is not important.
3. Replace argon bag in spectrometer. Bleed excess argon from bag if necessary. Close and lock rear cabinet.

7.3 Preparation for Power Outage

To prevent damage during power outages to the x-ray tube certain precautions shall be taken. Refer to EPA XRF SPECTROMETER USER'S GUIDE, VOLUME 1, Appendix A for this procedure.

7.4 Lab Environment

The laboratory space housing the spectrometer is temperature controlled to $70 \pm 2.0^{\circ}\text{F}$ with a relative humidity of 45%. These conditions are maintained by equipment located in the room. If malfunctions occur so as alter these conditions the spectrometer shall not be operated. The proper maintenance personnel shall be notified for repairs.

8.0 References

- 8.1 Barlow, P.M., LBL XRF Spectrometer User's Guide, Volume 1.
- 8.2 Waldruff, P., LBL XRF Spectrometer User's Guide, Volume 11.
- 8.3 Drane, E.A., et. al., Data Processing Procedures for Elemental Analysis of Atmospheric Aerosols by X-ray Fluorescence, Document TR-83-01 submitted under contract 68-02-2566.
- 8.4 Dzubay, T.G., et. al., Polymer Film Standards for X-ray Fluorescence Spectrometers, J. Trace and Microprobe Techniques, 5(4), 327-341, 1987-88.
- 8.5 Laboratory Notebook No. 888242, Issued to Thomas G. Dzubay, March 28, 1988.
- 8.6 Calibration Notebook, Located in S242J.

9.0 Appendix

9.1 Definitions

card files	-	an ASCII file created by LOTUS containing the field data and data processing options. Used in least squares analysis of spectra.
chi-square	-	a statistic which is a function of the sun of squares of the differences of the fitted and measured spectrum.
fluorescer	-	a secondary target excited by the x-ray source and in turn excites the sample.
fwhm	-	full width at half maximum, a measure of spectral resolution LBL - Lawrence Berkeley Laboratory.
NIST	-	National Institute of Standards and Technology.
nnnn	-	representation of an XRFID in a file name.
pp	-	representation of slot position in Argus slide tray.
run-time	-	during the operation of the spectrometer.
SARB	-	Source Apportionment Research Branch.
shape	-	the actual shape of a background corrected pulse height spectrum for an element.
SRMs	-	standard reference materials.
Teflo	-	trade name of a Teflon filter.
unknown	-	a sample submitted for analysis whose elemental concentration is not known.
xrf	-	x-ray fluorescence.

9.2 Derivation of -Effective Mass from NIST Certified Values

When NIST standards are analyzed no attenuation corrections are made even though such corrections are routinely made for aerosol samples. Also the NIST standards could not be mounted in the same plane as the calibration standards so an empirically determined geometric correction factor was determined to correct for this. Therefore, the attenuation and spacing corrections are applied to the standards by means of the below expression.

$$E=10000*MP/(AFZ)$$

Where:

E = effective mass (ng/cm²)
 M = total mass of standard film as measured by NIST (mg)
 P = % abundance supplied by NIST
 A = area of deposit (cm²) supplied by NIST
 F = attenuation correction supplied by NIST
 Z = spacing correction measured in XRF lab

SRM 1833

Serial No.: 882			Area (cm²): 10.06			Film Weight (mg): 1.658		
Element	Certified	%	F	Z	Effective	mass	(ng/cm²)	
Si	21.63	+-	1.4	1.14	1.043	29982	+-	1940
K	11.48	+-	1.1	1.07	1.050	16841	+-	1614
Ti	8.91	+-	1.2	1.04	1.061	13308	+-	1792
Fe	9.62	+-	0.3	1.02	1.153	13481	+-	420
Zn	2.16	+-	0.2	1.01	1.153	3057	+-	283
	9.03	+-	0.5	1.00	1.153	12908	+-	715
Pb								

SRM 1832

Serial No.: 1502			Area (cm ²): 10.06			Film Weight (mg): 1.650		
Element	Certified	%	F	Z	Effective	mass	(ng/cm ²)	
Al	9.27	+-	0.6	1.17	1.043	12459	+-	806
Si	21.39	+-	0.7	1.14	1.043	29506	+-	966
Ca	12.15	+-	0.8	1.04	1.050	18249	+-	1202
V	2.96	+-	0.3	1.02	1.061	4486	+-	455
Mn	2.83	+-	0.3	1.02	1.110	4100	+-	435
Co	0.65	+-	0.04	1.01	1.153	915	+-	56
Cu	1.49	+-	0.1	1.01	1.153	2099	+-	141

9.3 Results of SRM Analysis on 4/29/1992

SRM 1833				SRM 1832			
SI	30153.7	+-	2650.4	AL	13353.6	+-	1171.4
K	16289.8	+-	991.6	SI	27852.2	+-	2403.0
TI	13375.8	+-	1151.0	CA	18825.4	+-	1145.5
FE	13376.1	+-	1151.8	V	4591.4	+-	395.3
ZN	2932.4	+-	252.9	MN	4421.0	+-	270.0
PB	13277.6	+-	1142.7	CO	922.1	+-	80.3
				CU	2027.5	+-	175.0

9.4 Computer Menu

-----SELECTIONS-----

MAKE
SELECTION
AND
PRESS
ENTER

1. Run FPLOTT
2. Run DEBUG
3. Run CMD for testing basic XRF commands.
4. Test frames for sample changer compatibility.
5. Run XRF analyzer.
6. Least Squares Analysis of XRF Spectra
7. Format diskette on Drive A: (1 213 952 bytes)
8. Format diskette on Drive B: (362 496 bytes)
9. Check fixed disk
10. Add SRM 1833 & 1832 to archive
11. Run SUMBLK on blanks
12. Run BAKSUB on shapes standards
13. Plot spectra on screen
14. Convert spectra binary -> decimal & vice versa
15. Determine calibration factors
16. Run S & Cd QC standards
17. Archive XRF data
18. De-archive XRF data
19. Cross talk (Xtalk)
20. Upload data to VAX and print
21. Add last run's QC standards to archive (non-SRMs)
22. Check SRM data on selected XRFID
23. Print x-ray data to lab HP laser printer

9.5 Data Report on a Sample from a VAPS Sampler

SUMMARY: TELPLICE: 3/16 - 3/30

SITE	=	DTEP	SAMPLE DATE	=	3/20/92 AND 1900 HOURS
DURATION (MIN)	=	714.0	FLOW (L/MIN)	=	+-.500
FLOW FRAC	=	.0869			
XRF ID	=	148206	XRF ID	=	148256
SAMPLE ID	=	T0033	SAMPLE ID	=	MU0033

FINE, MG/M3				COARSE, MG/M3			
MASS	77912.	+-	1962.	MASS	11347.	+-	812.
*AL	162.2	+-	74.1	AL	539.9	+-	173.8
SI	213.4	+-	40.4	SI	909.5	+-	232.7
*P	12.1	+-	18.5	*P	-5.5	+-	11.3
S	2653.4	+-	183.7	7S	285.7	+-	84.9
CL	1164.4	+-	79.3	*CL	34.8	+-	24.6
K	193.6	+-	13.8	K	63.5	+-	8.9
CA	43.4	+-	5.6	CA	181.7	+-	13.9
*SC	3.6	+-	4.1	*SC	-1.3	+-	2.2
*TI	17.6	+-	6.6	TI	54.7	+-	9.6
*V	4.6	+-	2.3	*V	3.2	+-	1.7
*CR	2.0	+-	1.0	CR	9.8	+-	1.6
MN	10.0	+-	1.4	MN	10.1	+-	1.3
FE	243.7	+-	21.9	FE	783.5	+-	78.2
*CO	2.8	+-	1.8	*CO	4.8	+-	1.7
MI	3.8	+-	1.2	*MI	.3	+-	.6
CU	14.3	+-	1.9	CU	8.8	+-	1.3
ZN	167.5	+-	14.9	ZN	27.6	+-	4.9
*GA	2.4	+-	1.0	*GA	-.0	+-	.4
*GE	3.3	+-	1.3	*GE	.0	+-	.6
AS	24.7	+-	3.6	*AS	1.8	+-	1.2
SE	4.7	+-	.8	*SE	.7	+-	.4
BR	29.0	+-	2.8	BR	7.9	+-	1.1
*RB	1.7	+-	.8	*RB	1.0	+-	.4
SR	2.9	+-	.9	SR	2.2	+-	.5
*Y	12.4	+-	6.1	*Y	3.9	+-	2.9
*ZR	2.9	+-	4.8	*ZR	4.3	+-	2.6
*MO	7.3	+-	4.8	*MO	-3.2	+-	2.2
*RH	.0	+-	3.2	*RH	-1.2	+-	1.6
*PD	-3.6	+-	3.1	*PD	-1.0	+-	1.7
*AG	-6.4	+-	3.4	*AG	1.2	+-	1.9
*CD	8.5	+-	4.5	*CD	-.7	+-	2.2
SN	54.3	+-	9.4	*SN	2.3	+-	3.9
*SB	-1.6	+-	6.4	*SB	-.6	+-	3.3
*TE	2.5	+-	7.5	*TE	-7.2	+-	3.8
*I	25.0	+-	9.6	*I	2.4	+-	4.7
*CS	-4.0	+-	11.2	*CS	12.4	+-	3.9
*BA	-7.7	+-	13.7	BA	25.1	+-	7.4
*LA	-4.8	+-	34.5	*LA	22.6	+-	17.9
*W	-1.1	+-	2.6	*W	1.5	+-	1.3
*AU	-.9	+-	1.8	*AU	.2	+-	.9
*MG	-.4	+-	1.9	*MG	1.5	+-	1.0
PB	221.6	+-	19.7	PB	46.0	+-	6.2

* INDICATES THAT THE CONCENTRATION IS BELOW THREE TIME THE UNCERTAINTY.
XRF DATE = 04/29/1992 16:35 RBK (F): 04/29/1992 20:35 RBK

(C) SPECTRAL ANALYSIS DATE = 5/20/1992

9.6 Example SEM Format Data Report

FINE FILTER

XRFID = 148602
SAMPLE ID = T3001
FINE MASS (UG) = 240.0
FINE AREA (CM²) = 11.95
FINE LOADING (UG/CM²) = 20.1

COARSE FILTER

XRFID = 148652
SAMPLE ID = M3001
COARSE MASS (UG) = 270.0
COARSE AREA (CM²) = 11.95
COARSE LOADING (UG/CM²) = 22.6

ELEMENT	NG/CM ²	ASSUMED COMPOUND	WEIGHT %
*AL	-57.1 +-58.4	Al2O3	-.40 +- .41
SI	95.6 +-25.6	SiO2	1.02 +- .27
*P	12.6 +-12.9	P04	.19 +- .20
S	324.3 +-42.9	(NH4)2S04	6.66 +- .88.1
*CL	15.9 +- 7.8	NaCl	.20 +- 0
K	20.3 +- 5.1	K2O	.12 +- .03
CA	55.9 +- 7.7	CaCO3	.70 +- .10
*SC	-11.8 +- 4.8	Sc2O3	-.09 +- .04
*TI	8.4 +- 6.8	TiO2	.07 +- .06
*V	.9 +- 2.3	V2O5	.00 +- .02
*CR	2.9 +- 1.1	Cr2O3	.02 +- .00
*MN	.8 +- 1.1	MnO2	.00 +- .00
FE	218.7 +-20.2	FeO	1.40 +- .13
*CO	1.5 +- 2.6	CoO	.00 +- .02
*NI	1.1 +- 1.5	NiO	.00 +- .00
CU	15.8 +- 2.4	CuO	.10 +- .01
ZN	20.2 +- 2.6	ZnO	.13 +- .02
*GA	-1.7 +- 1.4	Ga	-.00 +- .00
*GE	-1.9 +- 1.7	Ge	-.00 +- .00
*AS	6.3 +- 5.2	As	.03 +- .03
*SE	-1.4 +- .9	Se	-.00 +- .00
BR	113.0 +-10.1	Br	.56 +- .05
*RB	-2.1 +- 1.4	Rb	-.01 +- .00
*SR	.9 +- 1.3	Sr	.00 +- .00
*Y	14.6 +- 6.7	Y	.07 +- .03
*ZR	-7.8 +- 4.7	Zr	-.04 +- .02
*MO	2.3 +- 4.8	Mo	.01 +- .02
*RH	-1.9 +- 3.4	Rh	-.00 +- .02
*PD	-4.2 +- 3.4	Pd	-.02 +- .02
*AG	-3.3 +- 3.7	Ag	-.02 +- .02
*CD	7.0 +- 4.8	CdO	.04 +- .03
SN	126.0 +-14.3	SnO	.71 +- .08
*SB	-11.3 +- 6.6	Sb	-.06 +- .03
*TE	6.1 +- 8.1	Te	.03 +- .04
I	49.8 +-11.1	I	.25 +- .06
*CS	-3.8 +-11.8	Cs	-.02 +- .06
*BA	9.8 +-14.6	Ba	.05 +- .07
*LA	-1.8 +-36.1	La	-.00 +- .18
*W	-7.1 +- 2.8	W	-.04 +- .01
*AU	5.0 +- 2.6	Au	.02 +- .01
*HG	.2 +- 2.8	Hg	.00 +- .01
PB	390.7 +-34.5	PbO	2.10 +- .19

ELEMENT	NG/CM ²	ASSUMED COMPOUND	WEIGHT %
*AL	408.2 +-182.7	Al2O3	2.56 +- 1.15
SI	2198.0 +-542.0	SiO2	20.81 +- 5.13
*P	53.0 +-29.2	P04	.72 +- .40
S	128.4 +-34.2	S04	1.70 +- .45
CL	162.9 +-21.2	NaCl	1.83 +- .24
K	172.9 +-17.7	K2O	.92 +- .09
CA	816.8 +-59.2	CaCO3	9.03 +- .65
*SC	-7.1 +- 5.5	Sc2O3	-.05 +- .04
TI	55.8 +-15.7	TiO2	.41 +- .12
*V	2.7 +- 3.9	V2O5	.02 +- .03
*CR	.0 +- 1.8	Cr2O3	.00 +- .01
MN	14.1 +- 2.2	MnO2	.10 +- .02
FE	1570.6 +-151.6	FeO	8.94 +- .86
*CO	-.5 +- 4.6	CoO	-.00 +- .03
*NI	3.0 +- 2.0	NiO	.02 +- .01
CU	94.3 +-10.3	CuO	.52 +- .06
ZN	59.1 +- 6.7	ZnO	.33 +- .04
*GA	1.2 +- 1.5	Ga	.00 +- .00
*GE	-3.7 +- 1.7	Ge	-.02 +- .00
*AS	2.6 +- 4.1	As	.01 +- .02
*SE	-1.9 +- 1.0	Se	-.00 +- .00
BR	53.1 +- 5.1	Br	.24 +- .02
*RB	2.0 +- 1.4	Rb	.00 +- .00
*SR	4.0 +- 1.5	Sr	.02 +- .00
*Y	4.7 +- 6.2	Y	.02 +- .03
*ZR	-3.5 +- 5.0	Zr	-.02 +- .02
*MO	4.2 +- 5.2	Mo	.02 +- .02
*RH	-6.5 +- 3.5	Rh	-.03 +- .02
*PD	.2 +- 3.8	Pd	.00 +- .02
*AG	6.9 +- 4.4	Ag	.03 +- .02
*CD	7.0 +- 5.0	CdO	.04 +- .03
SN	101.1 +-12.9	SnO	.51 +- .06
*SB	14.7 +- 7.8	Sb	.07 +- .03
*TE	-10.7 +- 8.5	Te	-.05 +- .04
*I	32.1 +-11.1	I	.14 +- .05
*CS	2.2 +-12.7	Cs	.00 +- .06
BA	92.7 +-18.3	Ba	.41 +- .08
*LA	46.1 +-39.8	La	.20 +- .18
*W	-3.9 +- 3.4	W	-.02 +- .02
*AU	-.4 +- 2.7	Au	-.00 +- .01
*HG	2.2 +- 3.1	Hg	.00 +- .01
PB	219.3 +-19.9	PbO	1.05 +- .09

Fraction of fine mass accounted for = .14

Fraction of coarse mass accounted for = .47

* INDICATES THAT THE CONCENTRATION IS BELOW THREE TIMES THE UNCERTAINTY

9.7 Detection Limits (16) for Teflo and Nuclepore Blank Filters

Teflo - fine		Nuclepore - coarse	
Element	DL ng/cm ²	Element	DL ng/cm ²
AL	55.0	AL	95.5
SI	17.3	SI	34.6
P	10.8	P	16.2
S	6.0	S	9.1
CL	4.8	CL	7.2
K	3.1	K	3.4
CA	3.4	CA	3.6
SC	3.3	SC	3.7
TI	5.0	TI	5.2
V	1.9	V	2.3
CR	1.0	CR	1.7
MN	1.1	MN	1.4
FE	2.2	FE	3.7
CO	1.5	CO	1.7
NI	1.2	NI	1.6
CU	1.0	CU	1.3
ZN	.8	ZN	.9
GA	.7	GA	.7
GE	1.1	GE	1.2
AS	1.1	AS	1.2
SE	.6	SE	.7
BR	.8	BR	.9
RB	.8	RB	.8
SR	.9	SR	1.0
Y	4.1	Y	4.0
ZR	3.7	ZR	3.7
MO	3.6	MO	3.9
RH	2.6	RH	2.6
PD	2.6	PD	2.6
AG	2.8	AG	2.9
CD	3.3	CD	3.5
SN	6.1	SN	6.1
SB	5.0	SB	5.1
TE	6.3	TE	6.3
I	7.1	I	7.3
CS	8.9	CS	8.8
BA	10.7	BA	10.7
LA	26.7	LA	27.6
W	2.0	W	2.0
AU	1.7	AU	1.8
HG	1.9	HG	1.9
PB	2.0	PB	2.1

These detection limits are interference-free and therefore ignore the effect of overlapping spectral lines on the light elements (postassium and lower). On an actual sample, the detection limit may be higher for these elements.

The difference in detection limits between the two filters is due more to the difference in sensitivity to fine and coarse particles and less to the difference in filter material.

Higher confidence levels may be chosen for the detection limits by multiplying the 1 σ limits by 2 for a 2 σ (or 95% level) or by 3 for 3 σ (or 99.7% level).

To convert the detection limits to more useful units, one can use the typical deposit areas for 37 mm and 47 mm diameter filters of 6.5cm³ and 12.0 cm², respectively.

9.8 Typical Run-time QC Results

08/14/1992 13:12 rbk

RESULTS FOR BOTTOM STANDARDS:

S	F	AREA	BACK	CHAN	FWHM	AREA	BACK	CHAN	FWHM
1	1 AL 58	35178.	5806.	28.88	6.1	-942.	4277.	79.43	.0
	LOWER LIMITS:	32640.	3944.	28.64	5.7	1107.	2089.	65.00	.0
	UPPER LIMITS:	37554.	7325.	29.00	6.5	-3322.	6267.	85.00	.0
151137.	SUMMARY:	OK	OK	OK	OK	OK	OK	OK	OK
2	1 S NTHP20	22416.	5850.	54.86	6.3	17.	3052.	.00	.0
	LOWER LIMITS:	20240.	4012.	54.54	5.9	-268.	1485.	65.00	.0
	UPPER LIMITS:	23287.	7450.	54.92	6.7	803.	4456.	85.00	.0
151138.	SUMMARY:	OK	OK	OK	OK	OK	OK	OK	OK
3	2 VK AERO1	26838.	4336.	86.91	8.1	24235.	2695.	137.25	6.1
	LOWER LIMITS:	24551.	2754.	86.61	7.6	22071.	1766.	137.01	5.7
	UPPER LIMITS:	28247.	5115.	87.09	8.6	25393.	3280.	137.37	6.5
151139.	SUMMARY:	OK	OK	OK	OK	OK	OK	OK	OK
4	3 FEPB 39B	39328.	1974.	182.09	6.9	50458.	13314.	375.34	7.7
	LOWER LIMITS:	34571.	1245.	181.85	6.5	45280.	8602.	375.13	7.2
	UPPER LIMITS:	39775.	2312.	182.27	7.3	52096.	15975.	375.59	8.2
151140.	SUMMARY:	OK	OK	OK	OK	OK	OK	OK	OK
5	4 ZRCD 38Y	37962.	3152.	700.67	11.3	28069.	1485.	472.35	8.8
	LOWER LIMITS:	33844.	2138.	700.42	10.6	25190.	1031.	472.13	8.3
	UPPER LIMITS:	38938.	3971.	701.10	12.0	28982.	1915.	472.65	9.3
151141.	SUMMARY:	OK	OK	OK	OK	OK	OK	OK	OK
6	8 SRM 1833	18361.	7718.	36.79	6.2	213058.	23562.	123.41	6.1
	LOWER LIMITS:	17207.	5304.	36.53	5.7	195242.	15604.	123.18	5.7
	UPPER LIMITS:	19797.	9850.	36.89	6.5	224633.	28978.	123.54	6.5

151142. SUMMARY:	OK	OK	OK	OK	OK	OK	OK	OK	OK
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RESULTS FOR BOTTOM STANDARDS:

S	F	AREA	BACK	CHAN	FWHM	AREA	BACK	CHAN	FWHM
1	1 AL 50	31159.	4361.	28.93	6.1	-143.	3080.	.00207	.9
	LOWER LIMITS:	29098.	3045.	28.64	5.7	-41.	1506.	65.00	.0
	UPPER LIMITS:	33478.	5655.	29.00	6.5	122.	4518.	85.00	.0
	151187. SUMMARY:	OK	OK	OK	OK		OK	OK	OK
2	1 S NTHP19	21232.	4941.	54.81	6.4	95.	2667.	.00148	2
	LOWER LIMITS:	19693.	3323.	54.54	5.9	-730.	1274.	65.00	.0
	UPPER LIMITS:	22658.	6172.	54.92	6.7	2190.	3822.	85.00	.0
	151188. SUMMARY:	OK	OK	OK	OK	OK	OK	OK	OK
3	2 VK AERO2	43761.	5716.	86.87	8.1	39176.	3828.	137.25	6.1
	LOWER LIMITS:	40352.	3807.	86.61	7.6	36052.	2430.	137.01	5.7
	UPPER LIMITS:	46427.	7070.	87.09	8.6	41479.	4514.	137.37	6.5
	151189. SUMMARY:	OK	OK	OK	OK	OK	OK	OK	OK
4	3 FEPB 31A	38593.	1953.	182.10	6.9	50043.	13209.	375.39	7.7
	LOWER LIMITS:	34921.	1271.	181.85	6.5	45828.	8743.	375.13	7.2
	UPPER LIMITS:	40178.	2360.	182.27	7.3	52727.	16237.	375.59	8.2
	151190. SUMMARY:	OK	OK	OK	OK	OK	OK	OK	OK
5	4 ZRCD 40A	41860.	3548.	700.74	11.3	31100.	1755.	472.38	8.8
	LOWER LIMITS:	37480.	2380.	700.42	10.6	28100.	1069.	472.13	8.3
	UPPER LIMITS:	43122.	4419.	701.10	12.0	32330.	1986.	472.65	9.3
	151191. SUMMARY:	OK	OK	OK	OK	OK	OK	OK	OK
6	8 SRM 1832	14358.	10651.	36.57	5.8	160051.	45676.	98.37	6.3
	LOWER LIMITS:	13773.	7304.	36.31	5.5	147811.	31874.	98.10	5.9
	UPPER LIMITS:	15846.	13564.	36.65	6.1	170062.	59194.	98.48	6.7
	151192. SUMMARY:	OK	OK	OK	OK	OK	OK	OK	OK

9.9 Assignment of XRFIDs Form

ASSIGNMENT OF XRFIDs											
FIRST 3 DIGITS	STUDY NAME & ARCHIVE ID	SUB-STUDIES									
		0	1	2	3	4	5	6	7	8	9

Assigner must enter data and initials each time a sub-study assignment is made.

XRF RUN STATUS LOG

[illegible]

SAMPLE CHECK-OUT LOG

[illegible]

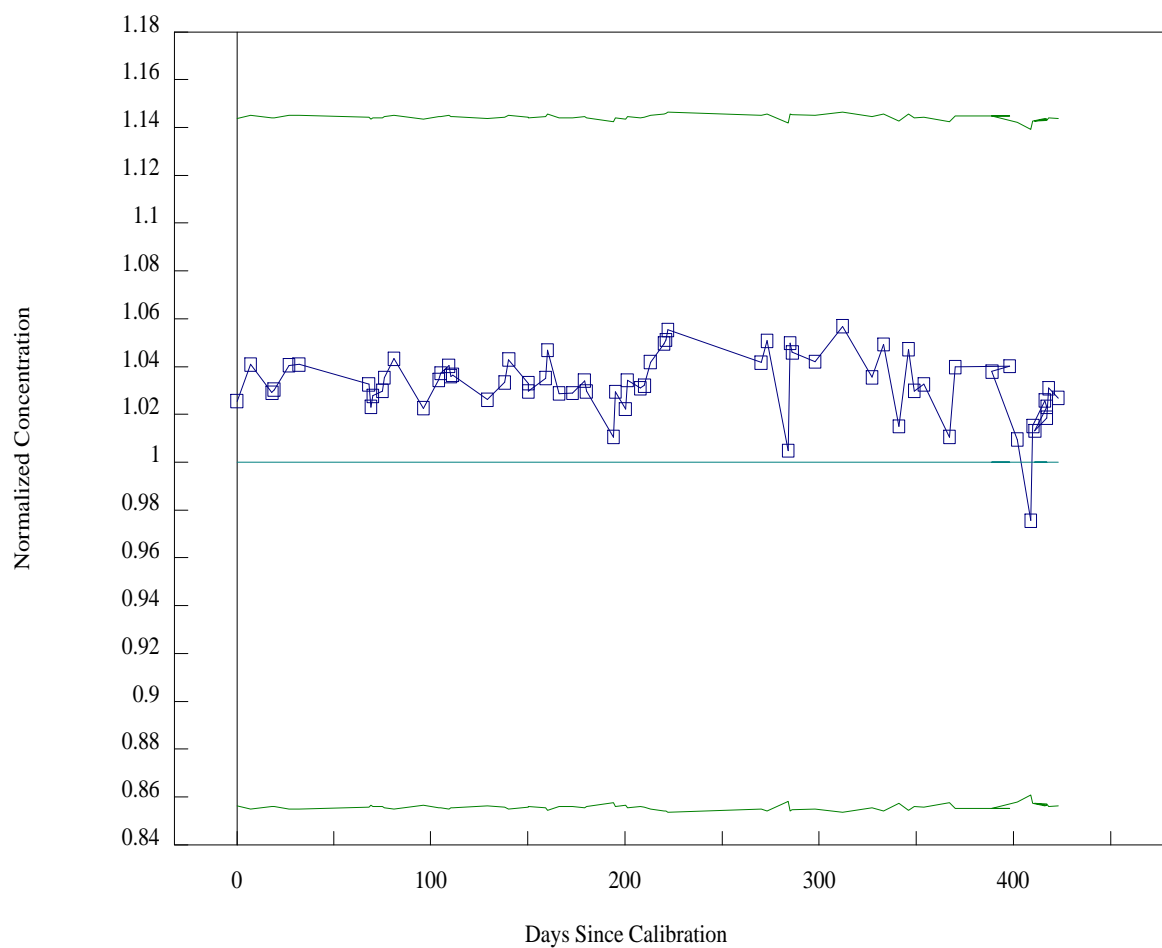
9.12 Calibration Standards and Concentrations

Standard ID	Element	µg/cm ²	Standard ID	Element	µg/cm ²	Standard ID	Element	µg/cm ²
Al 57	Al	57.0	TiGe29x	Ti	2.36	SrF2 13	Sr	12.8
Al 54	Al	54.0	V 45	V	45.0	SrF2 92	Sr	64.2
Al 63	Al	63.0	V 53	V	53.0	SrF2103	Sr	71.8
Al 29	Al	29.0	NiV21c	V	6.64	YF3 46	Y	28.0
Al 43.2	Al	43.2	Cr 30	Cr	30.0	ZrCd24c	Zr	9.85
Al 62	Al	62.0	Cr 53	Cr	53.0	ZrCd20w	Zr	10.77
Al 75	Al	75.0	Cr 85	Cr	85.0	MoO3145	Mo	96.7
SiO 46	Si	29.3	Cr 84	Cr	84.0	MoO3106	Mo	70.7
SiO 47	Si	29.9	Cr 75	Cr	75.0	MoO3110	Mo	73.3
SiO 51A	Si	32.5	Cr 74	Cr	74.0	MoO3 59	Mo	39.3
SiO 51B	Si	32.5	Cr 122	Cr	122.	MoO3 54	Mo	36.0
SiO 56	Si	35.7	CrCu32a	Cr	9.19	Rh 16	Rh	16.0
SiO 80	Si	51.0	CrCu26g	Cr	8.14	Pd 33	Pd	33.0
SiO27.6	Si	17.6	MnZn24b	Mn	8.57	Pd 198	Pd	198.0
SiO46.1	Si	29.4	Mn 57	Mn	57.0	Ag 35	Ag	35.0
SiO72.2	Si	46.0	Mn 183	Mn	183.	Ag 132	Ag	132.0
GaP 34	P	10.5	MnZn27x	Mn	9.10	Cd 83	Cd	83.0
GaP 40	P	12.3	FePb37y	Fe	7.72	ZrCd20w	Cd	9.15
GaP 70	P	21.5	Fe 107	Fe	107.0	ZrCd24c	Cd	8.38
GaP 105	P	32.3	Fe 127	Fe	127.0	Cd 77	Cd	77.0
CuS 13	S	13.0	Fe 46	Fe	46.0	Sn 40	Sn	40.0
CuS 33	S	33.0	Fe 88	Fe	88.0	Sn 185	Sn	185.0
NIST135	S	1.91	FePb38y	Fe	7.71	Sn 97a	Sn	97.0
NIST137	S	2.04	Co 45a	Co	45.0	Sn 97b	Sn	97.0
NIST138	S	2.14	Co 45b	Co	45.0	Sn 79	Sn	79.0
NIST140	S	2.31	RbCo29c	Co	7.43	Sb 194	Sb	194.0
NIST141	S	2.35	RbCo25b	Co	7.65	Sb 47	Sb	47.0
NIST143	S	2.30	Ni 54	Ni	54.0	Sb 147	Sb	147.0
NIST142	S	2.26	Ni 88	Ni	88.0	Sb 42	Sb	42.0
NIST139	S	2.30	NiV21c	Ni	5.77	SbSr29z	Sb	5.01
NIST136	S	1.76	Ni 101	Ni	101.0	SbSr31y	Sb	5.18
NIST134	S	1.77	Cu 96	Cu	96.0	Te 53	Te	53.0
NaCl 57	Cl	34.6	Cu 104	Cu	104.0	KI 46	I	35.2
NaCl 87	Cl	52.8	Cu 128	Cu	128.0	CsBr 53	Cs	33.1
NaCl 45	Cl	27.1	CrCu26g	Cu	7.65	CsBr 54	Cs	33.7
NaCl 72	Cl	43.4	CrCu32a	Cu	8.63	CsBr 51	Cs	31.9
KCl 45	Cl	21.4	Cu 38	Cu	38.0	BaF2108	Ba	84.6
KCl 53	Cl	25.4	Zn 51	Zn	51.0	BaF2 48	Ba	37.6
KCl 70	Cl	33.3	Zn 125	Zn	125.0	BaF2 60	Ba	47.0
KCl 45	K	23.6	MnZn27x	Zn	8.46	BaF2 57	Ba	44.7
KCl 53	K	28.0	MnZn24b	Zn	7.97	BaF2143	Ba	112.0
KCl 70	K	36.7	GaP 34	Ga	23.5	BaF2114	Ba	89.36
CaF2 37	Ca	19.0	GaP 40	Ga	27.7	BaAs23y	Ba	4.98
CaF2 29	Ca	14.9	GaP 70	Ga	48.5	BaAs36w	Ba	4.911
CaF2 90	Ca	46.2	GaP 105	Ga	72.7	LaF3157	La	111.3

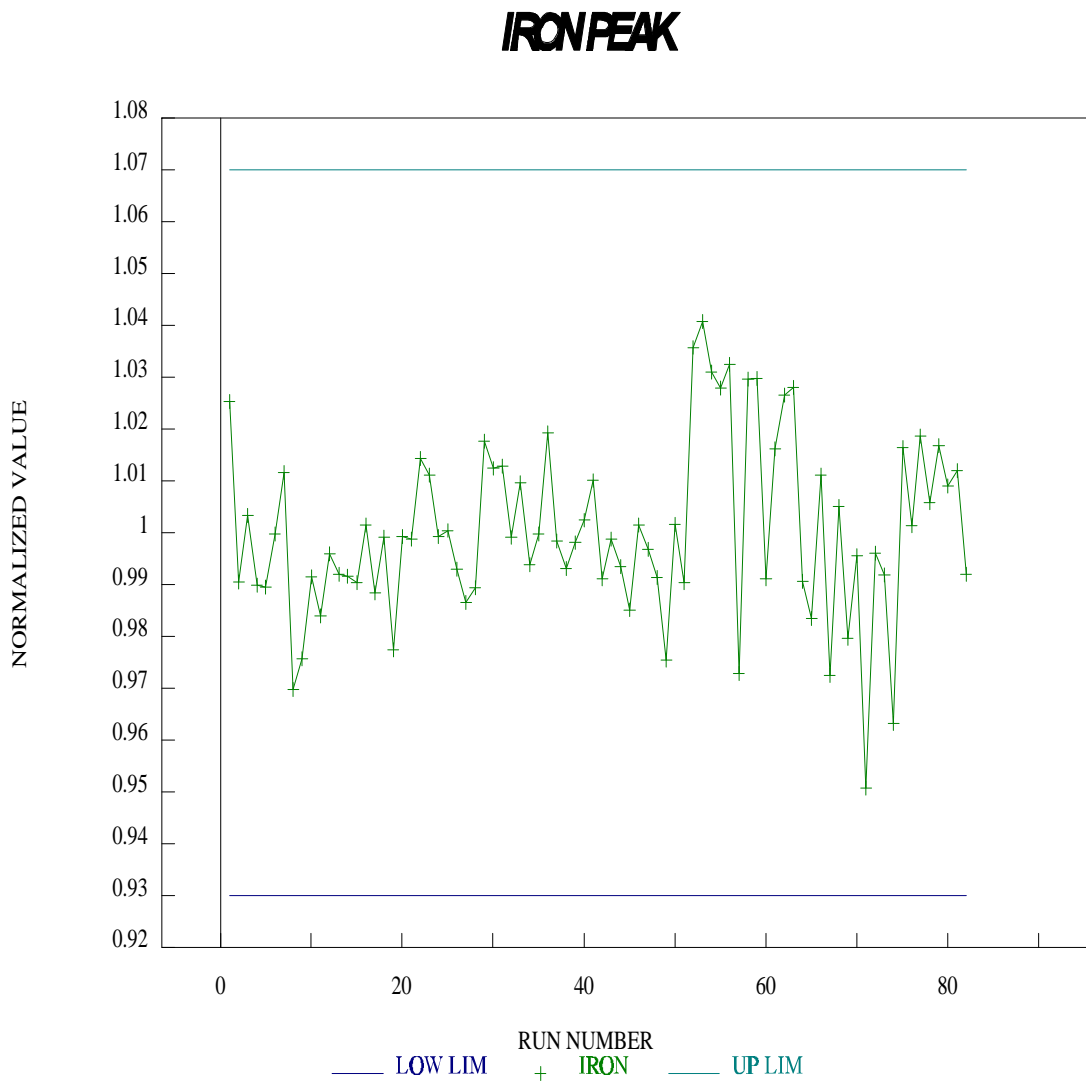
Standard ID	Element	µg/cm ²	Standard ID	Element	µg/cm ²	Standard ID	Element	µg/cm ²
CaF2 91	Ca	46.7	Ge 37	Ge	37.0	LaF3 62	La	44.0
CaF2102	Ca	52.4	TiGe29x	Ge	5.94	WO3 52	W	52.0
CaF2 66	Ca	33.9	TiGe33d	Ge	6.22	WO3 70	W	70.0
CaF2 28	Ca	14.4	Ge 140	Ge	140.0	WO3 58	W	58.0
CaF2 33	Ca	16.9	BaAs23y	As	5.60	Au 33	Au	33.0
CaF2 39	Ca	20.0	BaAs36w	As	5.521	Au 89	Au	89.0
CaF2 54	Ca	27.2	CsBr 53	Br	19.9	Au 62	Au	62.0
CaF2 29	Ca	14.9	CsBr 54	Br	20.3	Au 55	Au	55.0
CaF2 30	Ca	15.4	CsBr 51	Br	19.1	Au 45	Au	45.0
CaF2 52	Ca	26.7	RbNO346	Rb	26.6	Pb 67	Pb	67.0
CaF2 48	Ca	24.6	RbCo25b	Rb	7.88	Pb 55	Pb	55.0
CaF2 45	Ca	23.1	RbCo29c	Rb	7.65	Pb 118	Pb	118.0
CaF2 36	Ca	18.5	RbNO311	Rb	69.0	Pb 133	Pb	133.0
CaF2134	Ca	68.6	RbNO313	Rb	12.9	Pb 138	Pb	138.0
CaF2110	Ca	56.5	SrF2 57	Sr	39.8	Pb 64	Pb	64.0
ScF3 57	Sc	25.1	SbSr29z	Sr	4.97	FePb37y	Pb	7.47
Ti 39	Ti	39.0	SrF2 50	Sr	34.9	FePb38y	Pb	7.46
Ti 95	Ti	95.0	SbSr31y	Sr	5.14			
TiGe33d	Ti	2.46	SrF2137	Sr	95.6			

9.13 QC Chart for Pb in SRM 1833

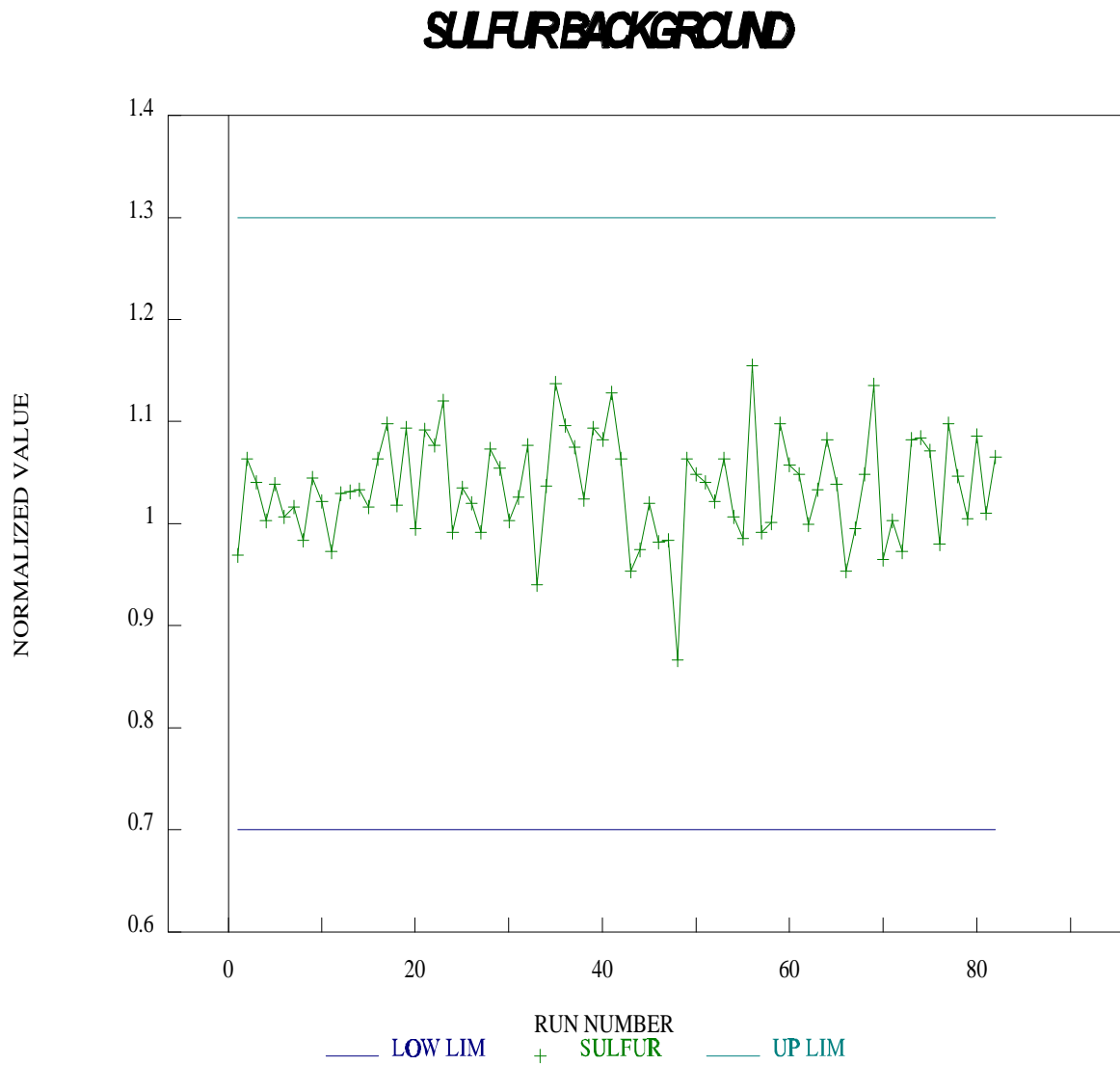
XRF Analysis of Pb in SRM 1833



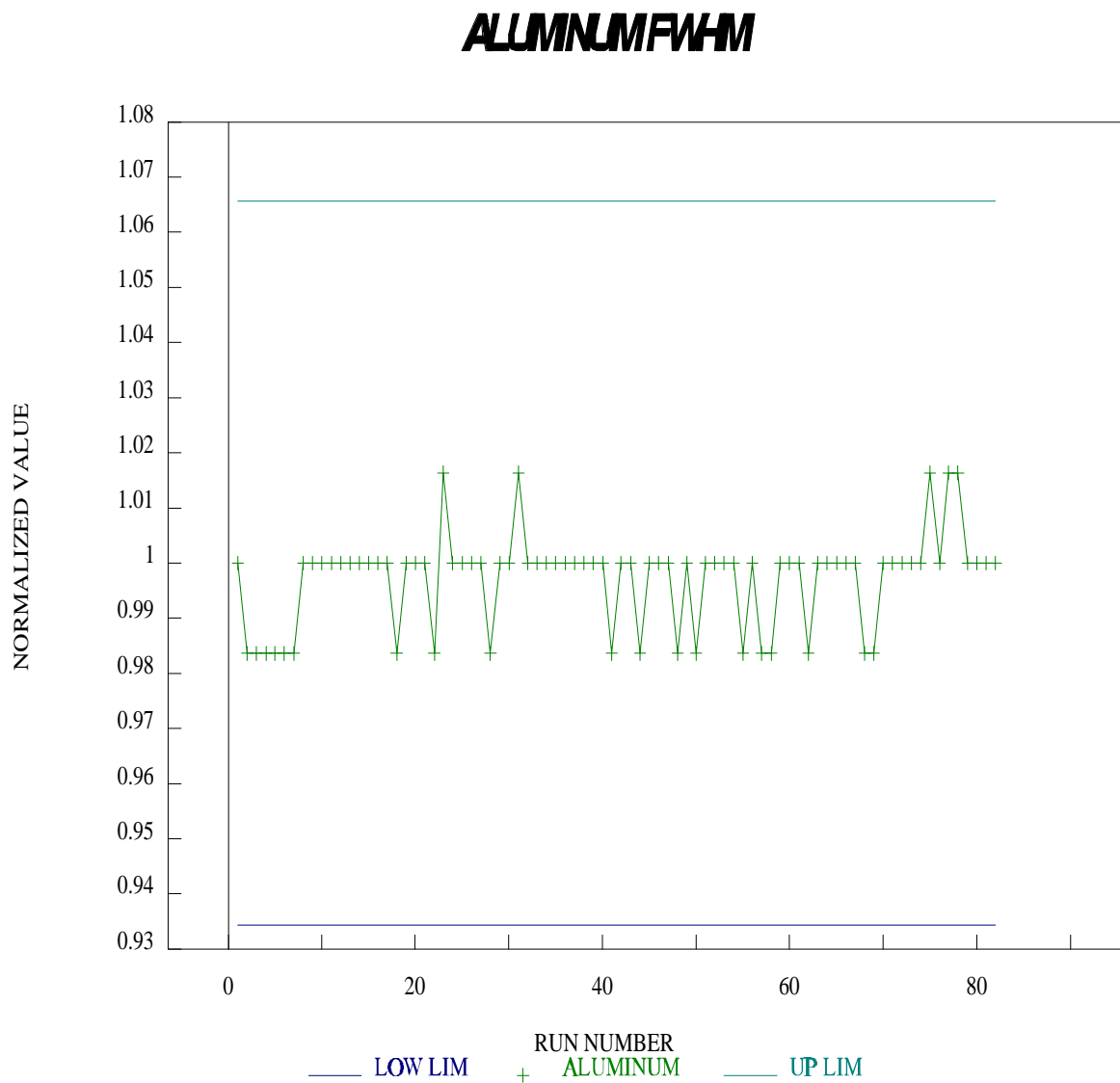
9.14 QC Chart for Fe Peak



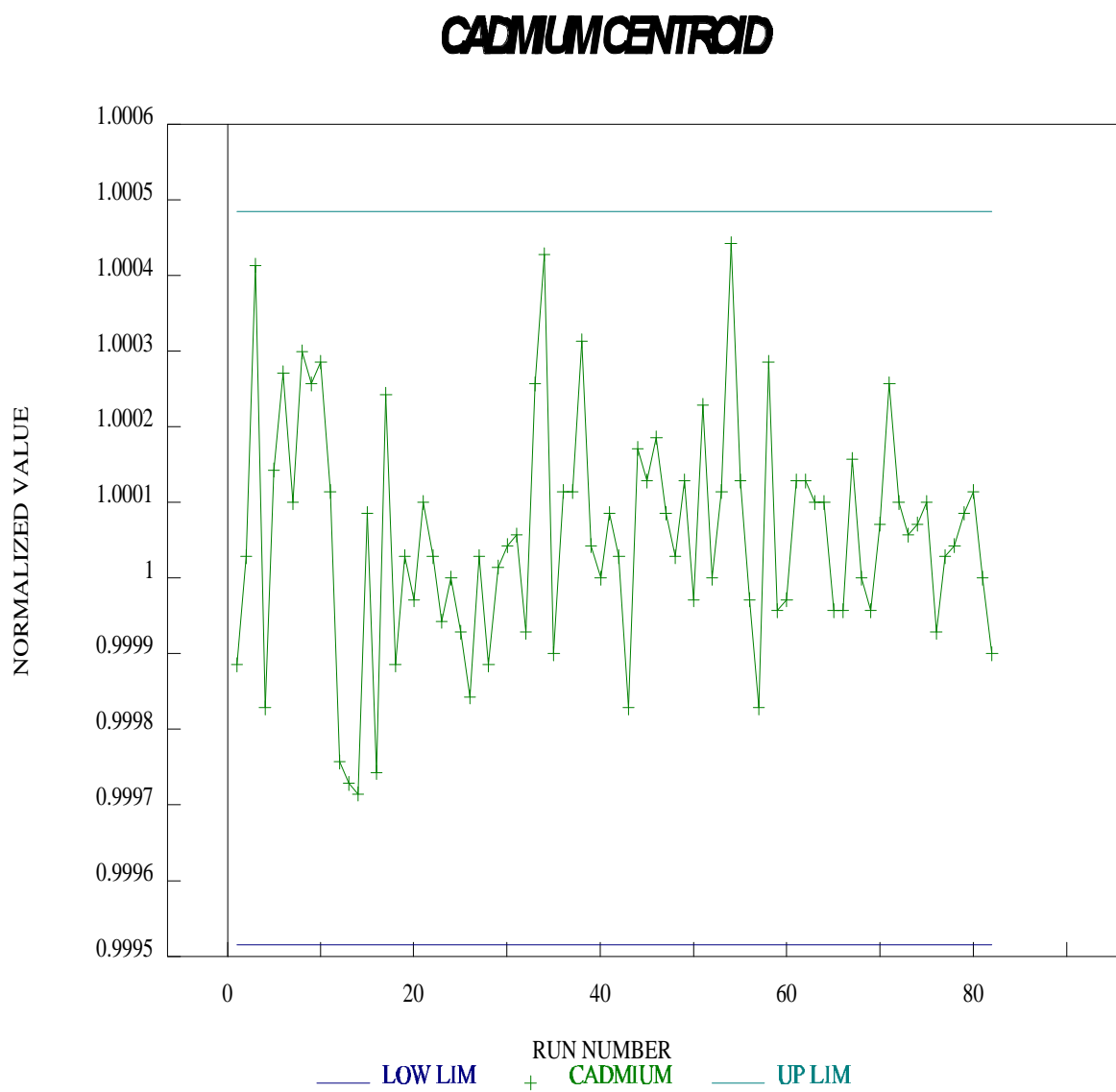
9.15 QC Chart for S Background



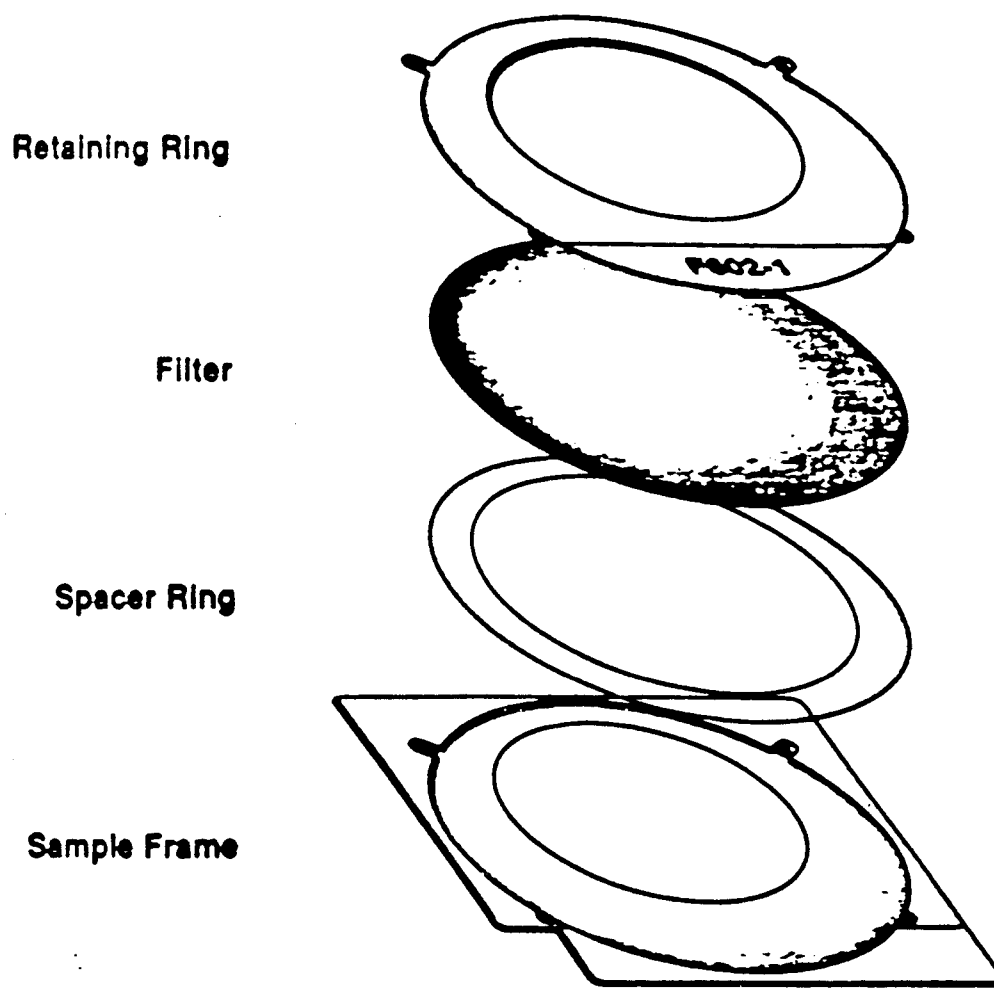
9.16 QC Chart for AL fwhm



9.17 QC Chart for Cd Centroid



9.18 Exploded View of Filter and Sample Frame Assembly



9.19 Creation of Lotus Spreadsheet Data

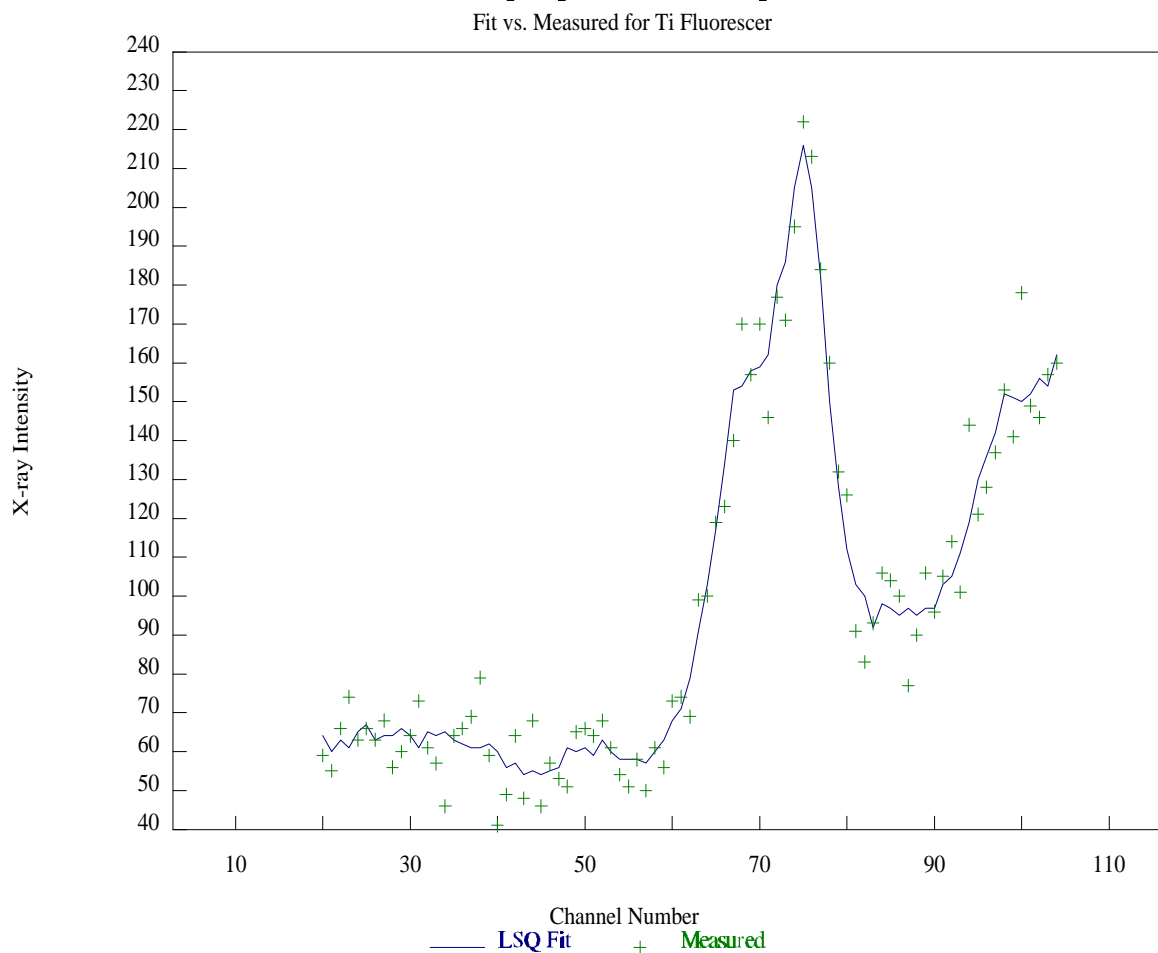
All data generated after Feb 27, 1992 and reported under the name LSQnnnn.NG3 can be put into spreadsheet form and reorganized under a different format. Reported with the data are two external files, NG3XTR8.EXE (a FORTRAN executable program requiring a math coprocessor) and REORG1.WK1 (a Lotus file Containing a macro). The program asks the user for the necessary information as needed. A hypothetical XRFID of 1111 will be used for illustration. To create the spreadsheet follow the instructions below. (User responses are in single quotes).

1. Type NG3XTRS from any directory
2. Enter file name 'LSQ1111.NG3'
3. Enter output file 'EXAMPLE.DAT'
4. Extract samples or blanks ISO (Here one makes a choice because both cannot be in same spreadsheet)
5. Enter output format 'S'
6. Uncertainty multiplier '3'
(Others may be chosen - see instructions in program. Remember the decimal. Program now begins extracting data from the file and creating output file).
7. Run Lotus and retrieve REORG1.WK1
8. Enter home. 'HOME'
9. Perform FILE/IMPORT/NUMBERS and import 'EXAMPLE.DAT'
10. Enter 'ALT S' and wait until execution finishes
11. Remember to save spreadsheet under a different name so as to not alter the original spreadsheet containing the macro.

9.20 Superposition of Fitted and Measured Spectrum

Regression Output:

9.13 Superposition of Spectra



Constant	4.50
Std Err of Y Est	9.34
R Squared	.956
No. Of Observations	85
Degrees of Freedom	83
X Coefficients(s)	.960
Std Err of Coeff.	.022